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13. ABSTRACT (Maximum 200 words) We have developed and characterized a broad class of synthetic metals and electroactive polymers. Refer to final technical report for AASERT grant F49620-93-1-0322 for an overview of advances made in transition metal complexes as radical anion components in synthetic metals. We have developed a new family of electrochromic polymers utilizing 3,4-ethylenedioxythiophene as an oxidatively polymerizable moiety. These polymers allow Band Gap Engineering such that the full visible spectrum is attained. These polymers have been incorporated into high contrast, dual polymer electrochromic devices which exhibit a high degree of switching stability (more than 10,000 switches easily attained). Luminescent polyphenylenes have been synthesized having both polar and ionic functionality. These have been incorporated into blue-emitting EL devices using electrostatic deposition methods. A number of external transitions with industry, Air Force personnel, and academic laboratories are underway researching applications for these polymers in electrochromic and electroluminescent devices, along with possibilities as corrosion protection coatings.				
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## Organic and Transition Metal Complex Superconductors and Redox Active Conductive Polymers

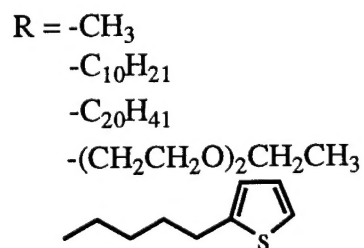
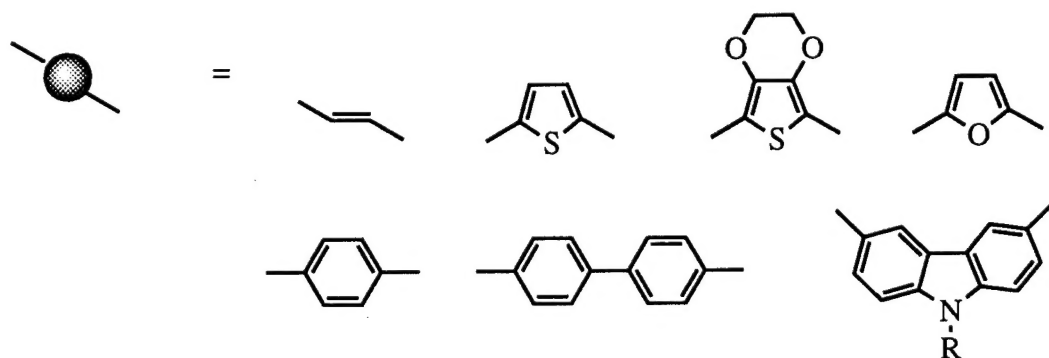
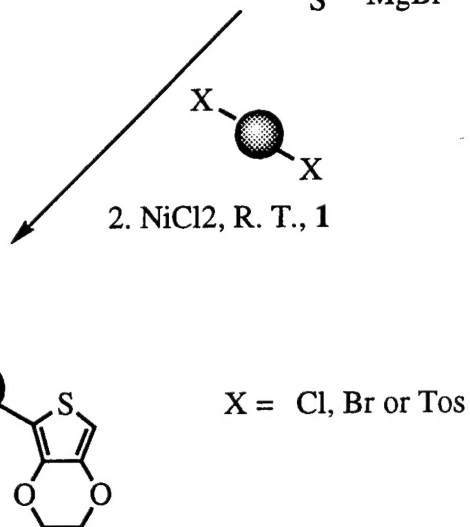
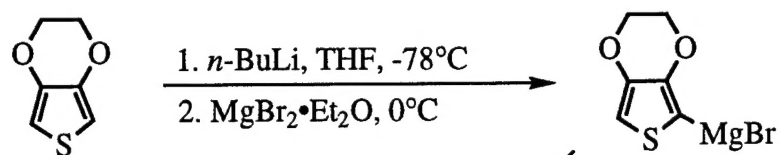
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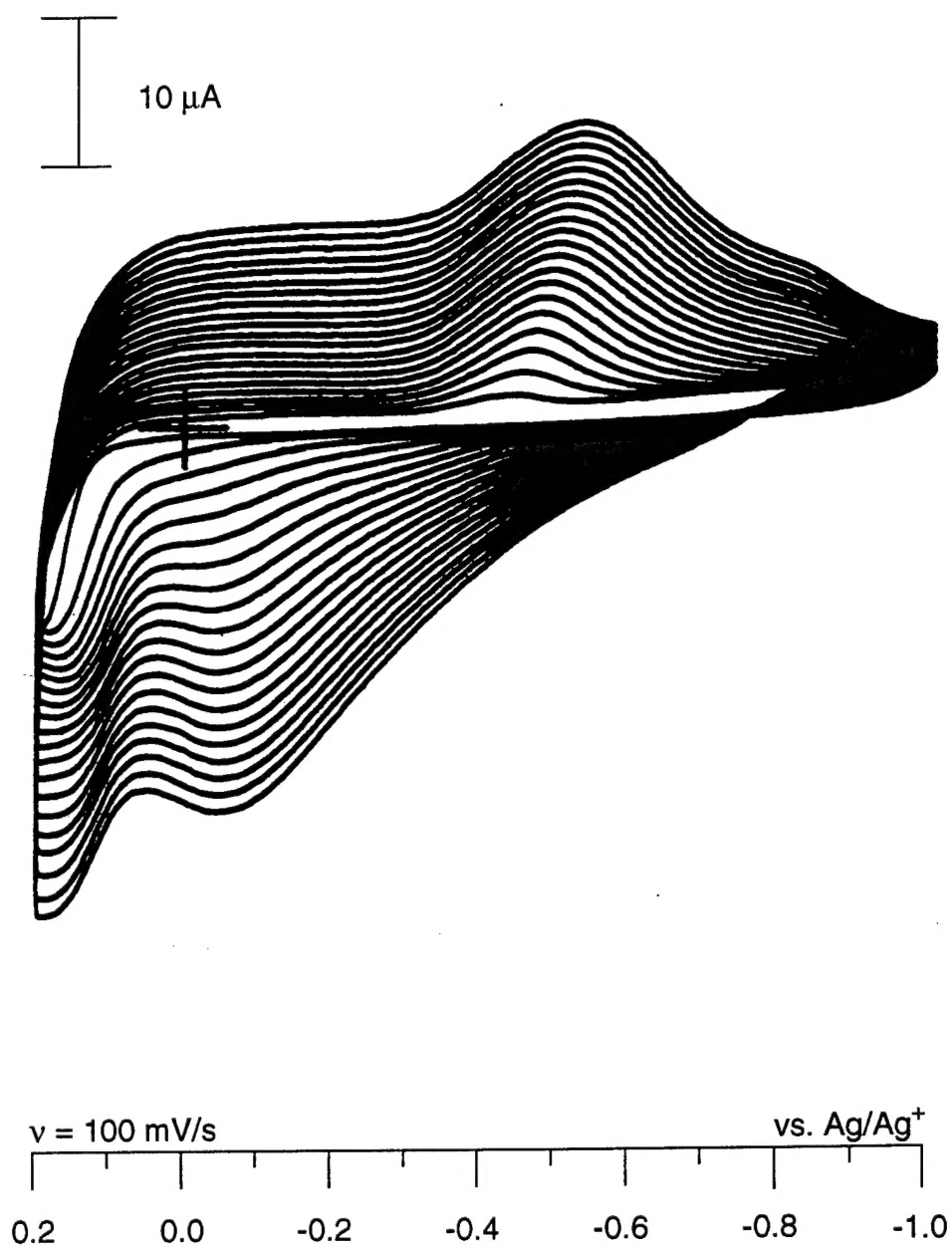
### Executive Summary

In this program, we have developed and characterized a broad class of synthetic metals and electroactive polymers. A final technical report has already been submitted for an AASERT grant that accompanied this grant (F49620-93-1-0322) and details successes in transition metal complex based molecular metals. Within the electroactive polymer work detailed below, significant advancement has been made in the synthesis and characterization of conjugated redox active polymers. Specifically we have developed a new family of electrochromic polymers that allow the full visible spectrum to be attained in dual polymer electrochromic devices. Luminescent polyphenylenes have been synthesized and incorporated into blue-emitting EL devices using electrostatic deposition methods. In the sections below, we highlight our most important advances. A number of external transitions with industry, Air Force personnel, and academic laboratories are underway and are listed on pages 13-14. This grant has been used to support 7 graduate students as researchers on various projects. A full listing of these researchers is given on page 14. A total of 30 presentations (many with conference proceedings) and 10 refereed publications resulted from this work. A full listing of these publications and presentations is given starting on page 15.

### Multicolor BEDOT-Based Electrochromic Polymers

A series of bis(2-(3,4-ethylenedioxy)thiophene) based monomers have been synthesized and fully characterized; specifically E-1,2-bis(2-(3,4-ethylene-dioxy)thienyl)vinylene (BEDOT-V), 1,4-bis(2-(3,4-ethylenedioxy)thienyl)benzene (BEDOT-B), 4,4'-bis(2-(3,4-ethylenedioxy)thienyl)biphenyl (BEDOT-BP), 2,5-bis(2-(3,4-ethylenedioxy)thienyl)furan (BEDOT-F), 2,5-bis(2-(3,4-ethylenedioxy)thienyl)-thiophene (BEDOT-T), 2,2':5',2''-ter(3,4-ethylenedioxy)thiophene (TER-EDOT), and a series of 3,6-bis(2-(3,4-ethylenedioxy)thienyl)-N-substituted carbazoles (BEDOT-NRCz). The general Scheme on page 2 depicts the synthesis of these monomers. These monomers oxidize and polymerize at low potentials relative to other reported electropolymerizable heterocycles. The cyclic voltammograms on page 3 show the repeated scanning electrochemical polymerization of TER-EDOT, the lowest oxidizing monomer of the series. The electroactive polymers formed exhibit low redox switching potentials and are quite stable in the conducting state. The electronic band gaps of these EDOT based polymers range from 1.4 eV to 2.5 eV (measured as the onset of the  $\pi$ - $\pi^*$  transition) offering a diverse range of colors which may prove useful in electrochromic devices. For example, poly(BEDOT-V) is deep purple and opaque in the reduced state and transmissive sky blue in the oxidized state, poly(BEDOT-T) is deep blue opaque in the reduced state and transmissive blue in the oxidized state, while poly(BEDOT-BP) is transmissive orange in the reduced state and opaque purple in the oxidized state. The series of BEDOT-NRCz's were found to exhibit three distinct colored states and could be rapidly and repeatedly switched between redox states.





## Cathodically Coloring Alkyl Derivatives of 3,4-Ethylenedioxythiophene (EDOT)

The synthesis of two new derivatives of 3,4-ethylenedioxythiophene (EDOT), specifically 5-octyldioxeno[2,3-c]thiophene (EDOT-C<sub>8</sub>) and 5-tetradecyldioxeno[2,3-c]thiophene (EDOT-C<sub>14</sub>), and their polymers has been accomplished. Cyclic voltammetry in 0.1M TBAP/CH<sub>3</sub>CN show irreversible monomer oxidation peaks ( $E_{p,m}$ ) at 0.89 V and 0.93 V respectively. Multiple scans yield electroactive and conducting polymer films on electrode surfaces. The PEDOT-C<sub>8</sub> and PEDOT-C<sub>14</sub> formed, oxidize with relatively low peak potentials at -0.22 V and -0.19 V respectively indicating the doped form of the polymer to be quite stable. Both PEDOT-C<sub>8</sub> and PEDOT-C<sub>14</sub> show two reduction processes with peaks at -0.18 and -0.16 V ( $E_{c1,p}$ ) and, -0.55 and -0.36 V ( $E_{c2,p}$ ) respectively. Optoelectrochemical studies reveal an  $E_g$  of 1.75 eV for both polymers. The polymers are electrochromic; relatively transmissive and light gray in the oxidized form while being opaque and deep purple in the reduced form exhibiting high electrochromic contrasts. Long term switching studies carried out in 0.1 M LiClO<sub>4</sub>/PC with Li/Li<sup>+</sup> as a reversible counter electrode process show that, PEDOT, PEDOT-C<sub>8</sub> and PEDOT-C<sub>14</sub> retained 65 %, 50 % and 62 % of their electroactivity after 6,000, 9,000 and 16,000 double switches respectively.

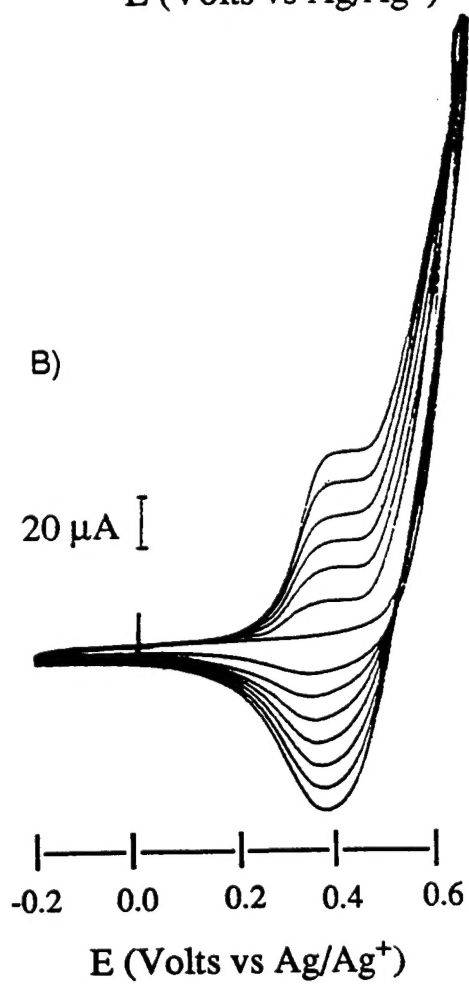
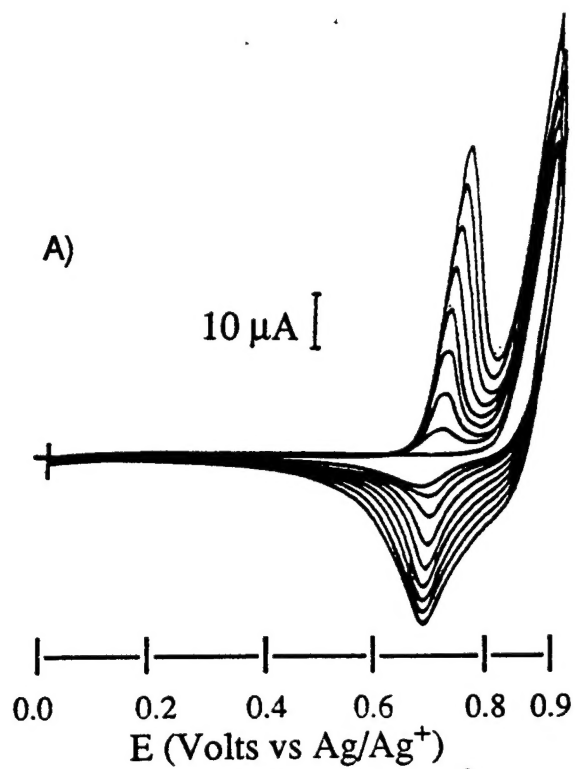
## Fluorene Derivatives as a Comparative Study of Reactivity

The monomers bis(2-thienyl)-9,9'-didecylfluorene, BTDF, and bis(2-(3,4-ethylenedioxy)thienyl)-9,9'-didecylfluorene, BEDOT-DF, have been synthesized by the group led by Dr. Bruce Reinhardt (WPAFB/MLPB) and electropolymerized to the corresponding conducting polymers. The electropolymerization and concurrent film deposition were carried out using multiple scan cyclic voltammetry. BTDF polymerizes efficiently in a solution 0.1 M TBAP in a 30:70 mixture of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN at 0.9 V vs Ag/Ag<sup>+</sup> as is shown in the Figure A on page 5. BEDOT-DF electropolymerizes at significant lower potentials and more rapidly than BTDF as can be observed in the Figure B. In this instance, the electropolymerization was carried out in 0.1 M TBAP/CH<sub>3</sub>CN as the monomer is soluble in CH<sub>3</sub>CN. The electron donating alkoxy substituents of the EDOT units lead to stabilization of the cation radical intermediates allowing the electropolymerization to proceed efficiently at 0.55 V.

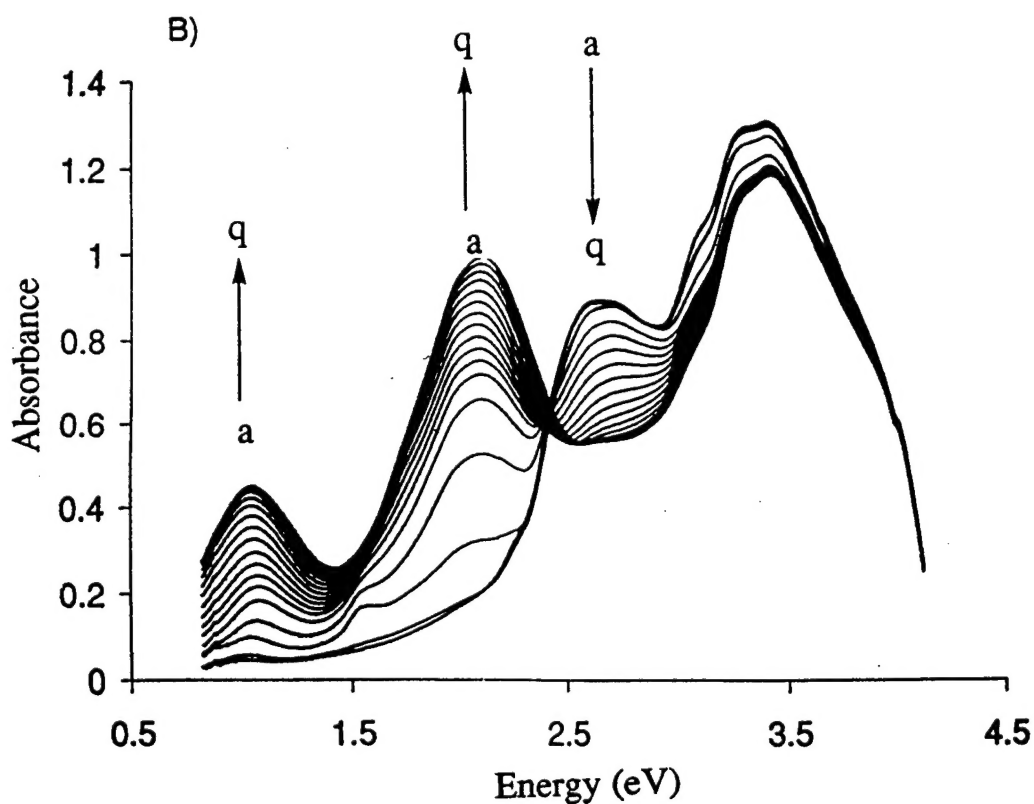
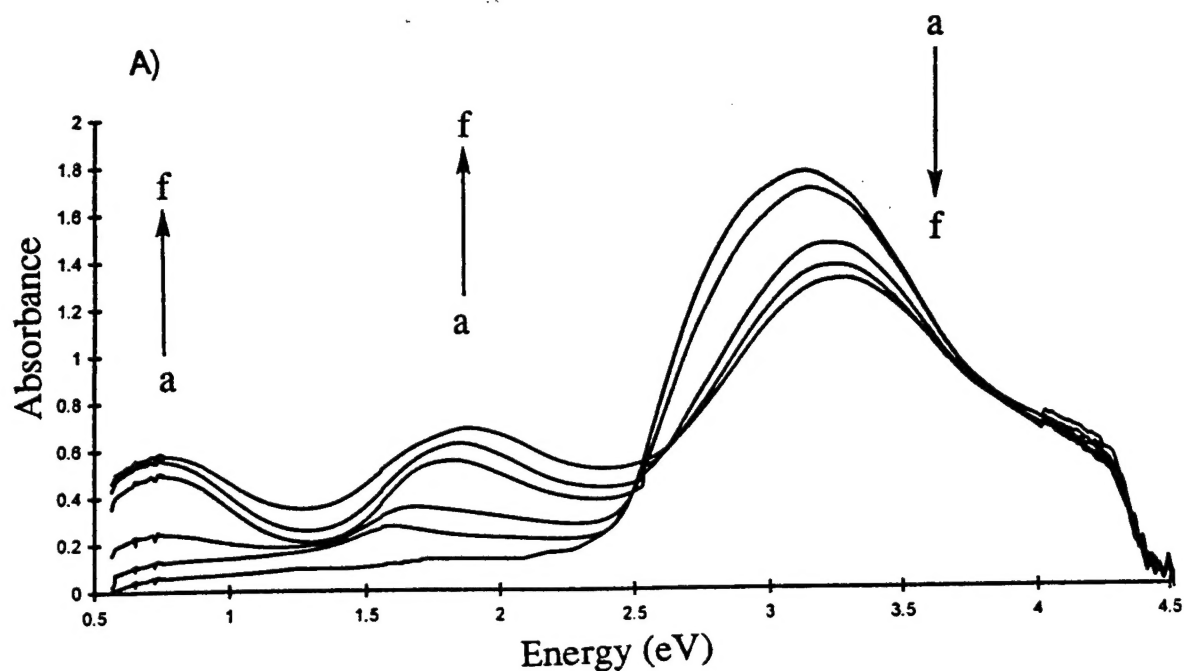
Cyclic voltammograms of the resulting PBTDF and PBEDOT-DF in monomer free electrolyte were carried out as a function of scan rate. Both the anodic and cathodic peaks scale linearly with scan rate for both polymers as it is expected for electrode supported electroactive films. The polymer redox potentials ( $E_{1/2}$ ) are 0.78 and 0.44 V for PBTDF and PBEDOT-DF respectively. The decrease in the  $E_{1/2}$  for PBEDOT-DF compared to PBTDF is the result of the increased electron density along the  $\pi$  system due to the presence of the alkoxy moieties of the EDOT units.

The electronic properties of PBTDF and PBEDOT-DF were studied by optoelectrochemistry after potentiostatic synthesis onto ITO glass electrodes. The spectra on page 6 were obtained as a function of potential. The band gaps are 2.4 and 2.2 eV for PBTDF and PBEDOT-DF respectively. Both polymers exhibited electrochemical and electrochromic reversibility and show polaronic states at intermediate doping levels.

The room temperatures conductivities for oxidized films of PBTDF and PBEDOT-DF are  $1 \times 10^{-4}$  and  $6 \times 10^{-4}$  respectively. Both polymers are insoluble in common organic solvents and they overoxidize rapidly when the applied potentials are 0.2 V higher than the  $E_{1/2}$  of the polymer.



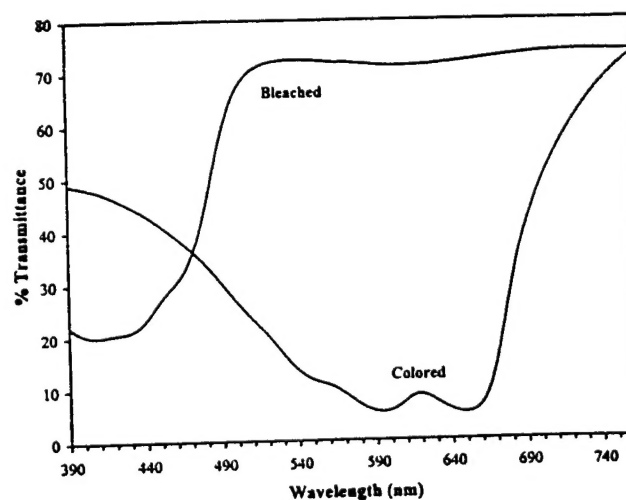
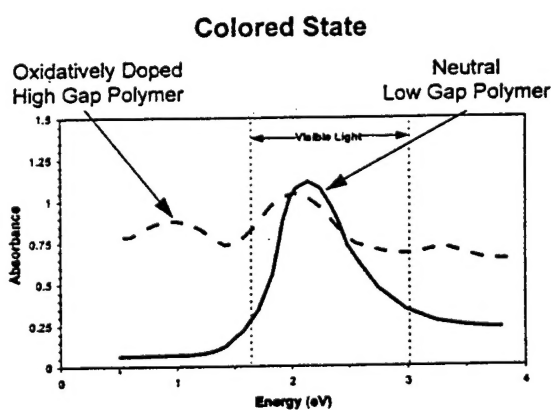
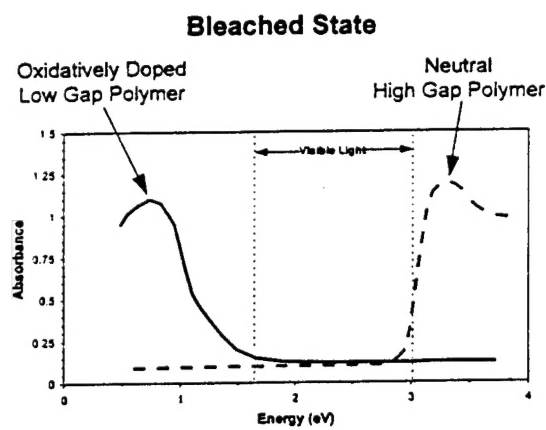
Multiple scanning polymerization of A) BTDF in 0.1 M TBAP/ $\text{CH}_2\text{Cl}_2$  (30:70). B) BEDOT-DF in 0.1 M TBAP/ $\text{CH}_3\text{CN}$ .



Optoelectrochemical analysis of A) PBTDF, spectra taken at a) 0.0, b) 0.50, c) 0.70, d) 0.80, e) 0.85, and f) 0.90 V. B) PBEDOT-DF, spectra taken at a) -0.5, b) -0.2, c) 0.0, d) 0.2, e) 0.25, f) 0.30, g) 0.34, h) 0.38, i) 0.40, j) 0.42, k) 0.44, l) 0.46, m) 0.48, n) 0.50, o) 0.52, p) 0.54, and q) 0.56 V vs Ag/Ag<sup>+</sup>.

## All Polymer Electrochromic Devices

Using the methodology described in the Scheme below, we have developed a series of high contrast electrochromic (EC) devices that exhibit sub-second switching times and useful lifetimes. We have studied twelve systems of EC devices based on complementary pairs of conducting polymer films. Combinations of four cathodically coloring polymers, base on 3,4-ethylenedioxythiophene (EDOT) and its alkylated derivatives, along with three anodically coloring polymers were employed in these devices. EC polymer films were obtained through electrochemical polymerization onto transparent indium doped tin oxide (ITO) glass electrodes. All polymer, solid state devices were constructed by combining these complementary pairs of EC polymer films together with a lithium salt and plasticized poly(methyl methacrylate) (PMMA) based polymer electrolyte. The devices reported here exhibited a wide range of  $\Delta\%T$  values in the range of 20-70% and response times for most devices were on the order of a few hundred milliseconds. This is illustrated by the Figure below which shows the visible transmittance spectrum for a hexadecyl derivatized PEDOT cathodically coloring polymer with poly[bis(3,4-ethylenedioxythiophene)-N-methylcarbazole] anodically coloring polymer device.



Visible Spectrum of Dual Electrochromic  
Polymer Device

Dual Electrochromic Polymer  
Device Concept



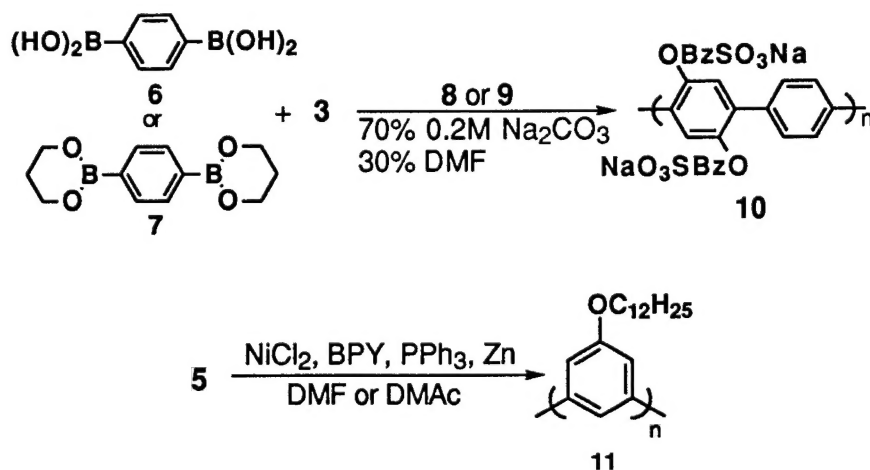
## Functionalized Poly(*p*-Phenylene)s as Luminescent Materials

### Alkoxy-Functionalized Poly(phenylenes)

The synthesis of derivatized polyphenylenes has been the focus of much attention as these polymers can possess many sought after properties such as a rigid-rod backbone, high thermal stability (of the neutral polymers), and an extended  $\pi$ -system, which can be both *p*- and *n*-doped. Of the side groups that can be affixed to the phenylene monomers, alkoxy-based units are highly useful due to their electron-donating nature and small steric hindrance. Unfortunately, while the alkoxy groups are ideal from a properties standpoint, they have proven to be synthetically difficult. The electron-donating effects of the alkoxy groups make the coupling of such substituted rings difficult by standard means.

We have developed the synthesis of two new alkoxy-substituted polyphenylenes, poly [2,5-bis(4-sulfonato-benzyloxy)-*alt*-1,4-phenylene] (PPP-(OBzSO<sub>3</sub>Na)<sub>2</sub>) and poly [3,5-(dodecyloxybenzene)] (PMP-OC<sub>12</sub>H<sub>25</sub>). PPP-(OBzSO<sub>3</sub>Na)<sub>2</sub> was obtained by the Pd(0) catalyzed cross-coupling of 1,4-dibromo-2,5-bis(4-sulfonatobenzyloxy) benzene disodium salt with 1,4-benzenediboronic acid or 1,4-benzenediboronic acid-propyldiester under basic conditions (~pH 12) as shown in the Scheme below. The palladium catalyst used in polymerization was either palladium acetate **8** or the water soluble (Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-*m*-SO<sub>3</sub>Na]<sub>3</sub> **9**. Both catalyst and monomer types were varied to investigate their respective effects on polymerization. UV-Vis absorption was used as the criterion for assessing extent of polymerization (the higher the absorption maximum, the better the polymerization), and the best conditions were found to include the use of **3** with **6** and **8**.

PMP-OC<sub>12</sub>H<sub>25</sub> was obtained from 3,5-dichlorododecyloxybenzene utilizing a homocoupling polymerization, which employs a nickel catalyst / zinc reduction system also illustrated in the Scheme below. Solvents and catalyst amount were varied with hopes of gaining insight into this polymerization; however, molecular weight studies of the corresponding polymers showed no significant differences between runs.



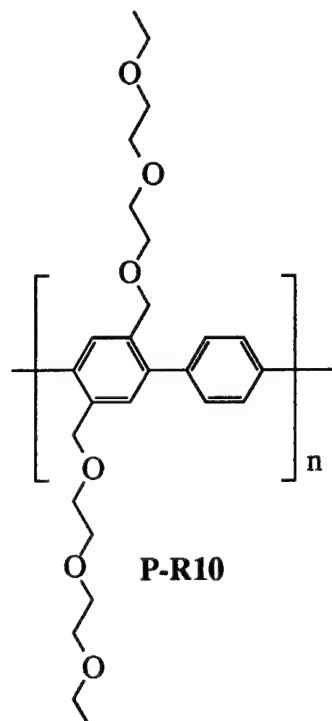
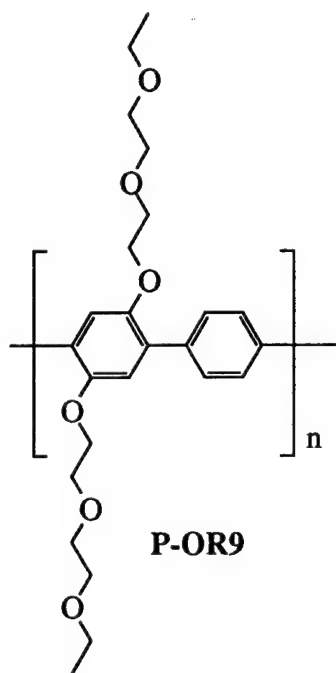
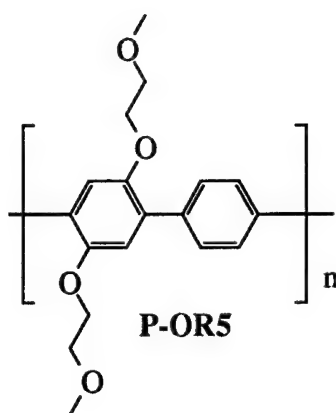
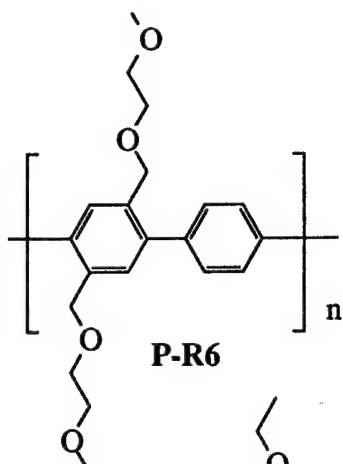
Thermal analyses show that these are well behaved polymers, stable to over 300°C. Unfortunately, no molecular weight information could be obtained on the PPP-(OBzSO<sub>3</sub>Na)<sub>2</sub>. The ionic groups of the rigid-rod polyelectrolyte had strong interactions with gel permeation chromatography (GPC) columns and made vapor pressure osmometry (VPO) impossible. The polymer's strong luminescence also precluded investigation by light-scattering techniques. However, the PMP system was much more accommodating for obtaining molecular weight information. Chloroform GPC of **11** showed a monomodal distribution with  $M_n = 9725$  and Poly Dispersity Index (PDI) = 2.12 relative to polystyrene standards. Toluene VPO of the same polymer at 50°C gave an  $M_n = 8800$ , which is in relatively good agreement with GPC data. Matrix Assisted Laser Desorption Ionization-Mass Spectrometry (MALDI-MS) displayed peaks corresponding to the 260 g/mol repeat unit up to 12,000 g/mol. All of the molecular weight data for **11** seem to indicate an average structure with approximately 40 rings per chain.

One of the primary goals for each of the different systems was to investigate the polymer's electronic properties. Both of these materials exhibited strong solution fluorescence when excited by a Xenon lamp at 313 nm. The PPP derivative is a blue emitter ( $\lambda_{max} = 420$  nm) while the PMP polymer emits mostly in the UV region ( $\lambda_{max} = 346$  nm) with only a weak violet emission observable by the naked eye.

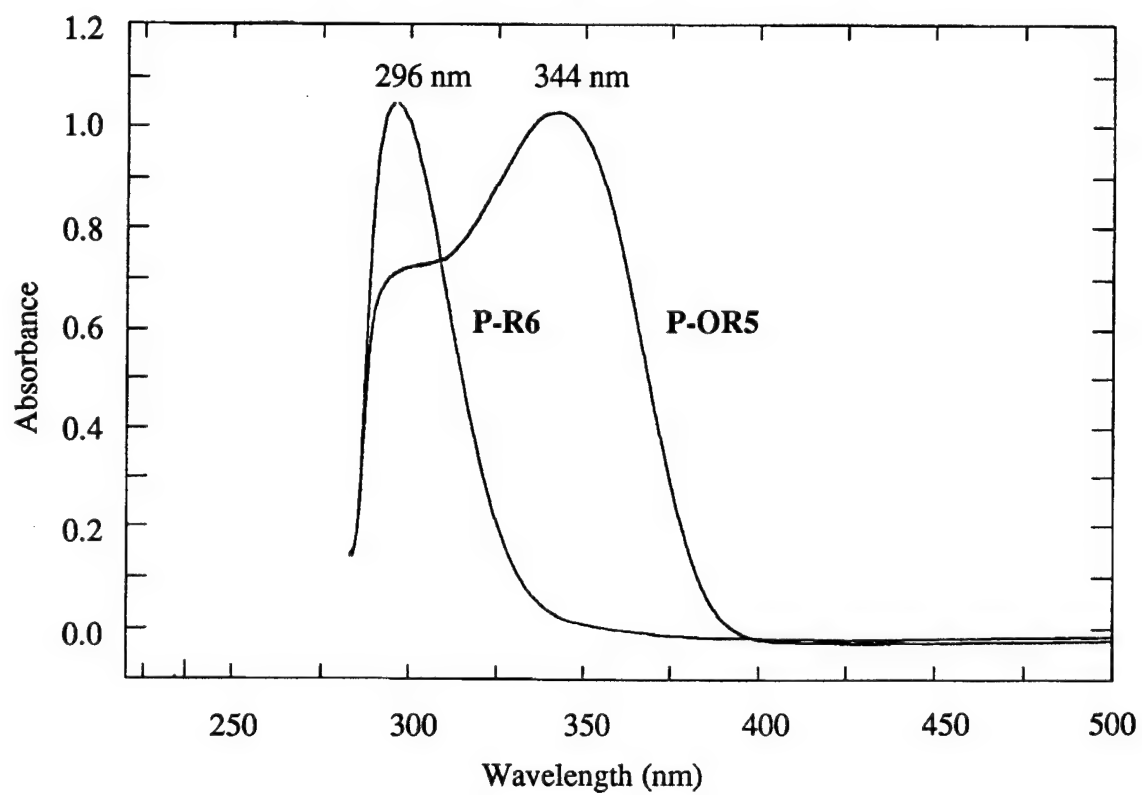
We have synthesized poly(*p*-phenylene)s (PPP's) with cationic sidechains, and PPPs with cation coordinating sidechain for possible use in light emitting devices. The PPPs with cation coordinating sidechains are illustrated by the structures shown on page 10.

These methoxyethoxy- and triethoxy- substituted PPPs have physical and electronic properties which are dependent upon the nature and length of the sidechain, as well as upon molecular weight. The short sidechains of **P-OR5** and **P-R6** afford a lower degree of solubility and so lower degrees of conjugation--hence they display lower  $\lambda_{max}$  than their longer chain counterparts, **P-OR9** and **P-R10**. The lower molecular weight (10-15 rings) allows the oligomers of **P-OR5** and **P-R6** to be processed by vapor deposition, while polymers of **P-OR9** and **P-R10** tend to be soluble and processable by solution methods. Large differences in electronic properties are found between the P-OR and P-R series, as can be seen in the absorption spectra of **P-OR5** and **P-R6** shown on page 11.

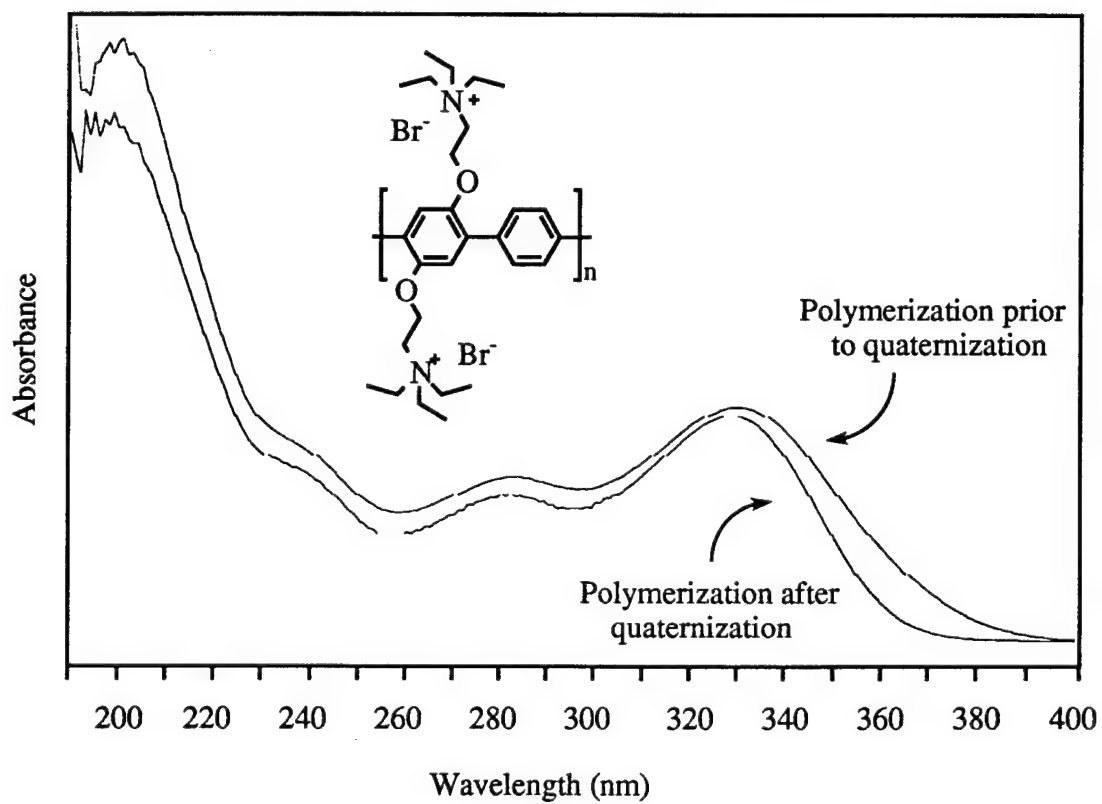
Tetraethylammonium substituted PPPs were synthesized via Suzuki polymerization. Organic soluble polymers were obtained via the polymerization of neutral tertiary amine monomers. These polymers are soluble in aqueous acid. Likewise the polymers were fully quarternized, upon which they attained water solubility. Quaternary PPPs were also synthesized via the polymerization of quaternary monomers. Spectra for polymers prepared by both methods are shown on page 12. The latter method offers no advantage, since the resultant polymers contain residual salts which are difficult to remove.



### UV-Vis of Dialkyl and Dialkoxy-PPP's



### Electronic Absorption Spectrum of PPP-OEt<sub>4</sub><sup>+</sup> Br<sup>-</sup>



## Transitions

### 1. WPAFB/WL-MLP-Patrick Hood

Discussions with Dr. Hood have discerned there is interest on both our sides in developing further interactions with possibilities in laser protection. Dr. Reynolds will be presenting a seminar to this group on October 23, 1996.

### 2. WPAFB-MLPB/Dr. Bruce Reinhardt

The Reinhardt group has prepared a set of bis(2-thienyl) and bis(2-EDOT) functionalized dialkyl fluorene monomers. The electronic properties of the polymers were studied by optoelectrochemistry after potentiostatic synthesis onto ITO glass electrodes. A full paper is presently being prepared for submission to the *Journal of Polymer Science*.

### 3. WPAFB-MLPB/Dr. Doug Dudis

Graduate student David Irvin, participated in a summer exchange program, spending ten weeks in Dayton interacting with WPAFB researchers. His work is detailed in the following:

In order to tune the band gap and to attain high band gap polymers with low oxidation potentials (high HOMO), and subsequently to tune the electrochromic properties, monomers and polymers containing electron withdrawing were synthesized and modeled by AM1 and *ab initio* methods. Our results indicate that the calculated change in HOMO-LUMO gap energy, between the monomer and the polymer, are within 0.2 eV of experimental measurements.

### 4. Ohio State/Professor Art Epstein

Two samples of electron rich, soluble and processable, conducting polymers based on EDOT have been submitted to the Epstein group for corrosion protection studies. Initial results indicate that some corrosion protection of steel is afforded by these materials and further work is warranted. These studies are being continued.

### 5. MIT/ Professor Michael Rubner

The Rubner group continues to study the water soluble luminescent polymers we are synthesizing. Electrostatic deposition methods are used to make LED's and to study charge transfer between conducting polymer layers.

### 6. Monsanto Inc./Dr. Jim Coleman

Monsanto has made a large commitment to conducting and electroactive polymers over this last year. This includes the purchasing of 78 patents along with all of the rights to market the Allied developed polyaniline product Versicon. Within this program, Monsanto is interested in electromagnetic shielding, anti-stat, corrosion protection, electrochromics, and active molecule delivery.

Based on the high degree of control of the redox and optical properties we have developed in our polymers, Monsanto has taken a strong interest in our work. We have exchanged visits and are presently pursuing joint research efforts. These are in the areas of multi-color electrochromic displays (mainly for advertising applications, but potentially useful

for chameleon materials) based on our electrochromic polymers and in the release of biologically active chemicals.

#### 7. Gentex Inc./Dr. Tom Guarr

Gentex is the worlds largest supplier of electrochromic mirrors for automotive applications. In 1996 they expect to sell about 3 million units. Presently, the Gentex system is based on a soluble electrochromic molecule dissolved in a polymer gel. Gentex is highly interested in the electrochromic polymers developed at the University of Florida as they provide opportunities for multi-color systems not presently accessible with Gentex technology, and they are significantly faster in their redox switching times.

#### Personnel Supported

The following Graduate Research Assistants were supported by this grant.

Peter Balanda	presently at UF
David Irvin	presently at UF
Jennifer Irvin	presently at UF
Seungho Kim	working in Korea
Jerry Reddinger	presently at UF
Bala Sankaran	postdoctoral fellow at WPAFB/MLPB
Greg Sotzing	presently at UF

## Refereed Publications Resulting From This Grant

Musfeldt, J. L., Reynolds, J. R., Tanner, D. B., Ruiz, J. P., Wang, J., and Pomerantz, M.  
*J. Polym. Sci., Polym. Phys. Ed.*, **32**, 2395-2404 (1994).

"Luminescent Polymers with Discrete Emitter Units"

Demoustier-Champagne, S., Reynolds, J. R. and Pomerantz, M.  
*Chem. Mater.*, **7**, 277-283 (1995).

"Charge and Ion Transport Properties of Polypyrrole/Poly(styrene sulfonate): Poly(3-octylthiophene) Bilayers"

Sotzing, G. A. and Reynolds, J. R.  
*J. Chem. Soc., Chem. Commun.*, 703-704 (1995).

"Poly[*trans*-bis(3,4-ethylenedioxythiophene)vinylene]: A Low Band Gap Polymer with Rapid Redox Switching Capabilities Between Conducting Transmissive and Insulating Absorptive States"

Piotraschke, J., Pullen, A. E., Abboud, K. A. and Reynolds, J. R.  
*Inorg. Chem.*, **34**, 4011-4012 (1995).

"Extensively Conjugated Bimetallic (m-Tetrathiooxalato) Copper (II) Complex (Bu<sub>4</sub>N)<sub>2</sub> [(C<sub>3</sub>S<sub>5</sub>)CuC<sub>2</sub>S<sub>4</sub>Cu(C<sub>3</sub>S<sub>5</sub>)] for Electrically Conducting Charge Transfer Complexes"

Child, A. D., Sankaran, B., Larmat, F. and Reynolds, J. R.  
*Macromolecules*, **28**, 6571-6578 (1995).

"Charge Carrier Evolution in Electrically Conducting Substituted Polymers Containing Biheterocycle/*p*-Phenylene Repeat Units"

Pullen, A. E., Piotraschke, J., Abboud, K. A., Reynolds, J. R.  
*Inorg. Chem.*, **35**, 793-796 (1996)

"The Preparation, Structure and Properties of an Anionic Tetrameric Copper Complex Containing a Planar, Eight-Membered Ring Core"

Kim, S., Cameron, D. A., Lee, Y., Reynolds, J. R. and Savage, C. R.  
*J. Polym. Sci., Polym. Chem. Ed.*, **34**, 481-492 (1996).

"Aromatic and Rigid Rod Polyelectrolytes Based on Sulfonated Poly(benzobisthiazoles)"

Sotzing, G. A., Reynolds, J. R. and Steel, P. J.  
*Chem. Mater.*, **8**, 882-889 (1996).

"Electrochromic Conducting Polymers via Electrochemical Polymerization of Bis(2-(3,4-ethylenedioxy)thienyl) Monomers"

Liu, H. L., Tanner, D. B., Pullen, A. E., Abboud, K. A. and Reynolds, J. R.  
*Phys. Rev. B*, **53**, 10,557-10,568 (1996).

"Optical and Transport Studies of Ni(dmit)<sub>2</sub> Based Organic Conductors"

Pullen, A. E., Zeltner, S., Olk, R.-M., Kirmse, R., Hoyer, E., Abboud, K. A., Reynolds, J. R.  
*Inorg. Chem.*, **35**, 4420-4426 (1996).

"Extensively Conjugated Dianionic Tetrathiooxalate Bridged Copper (II) Complexes for Synthetic Metals"



## Presentations and Conference Proceedings Resulting From This Grant

Materials Research Society, 1993 Fall Meeting, Boston, MA, November 1993

"Optical Absorption, Luminescence and Redox Switching Properties of Polyphenylene Derivatives" with A. D. Child, J. R. Ruiz, J. L. Musfeldt, B. Sankaran, F. Larmat, P. Balanda and D. B. Tanner, *Mats. Res. Soc. Symp. Proc.* **328**, 191-195 (1994).

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